

Evaluating Anthropogenic Impact on Water Quality of Ohio Rivers Over Time

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Abstract

Natural and anthropogenic factors affect the geochemistry of rivers and streams in both rural and urban areas. Much of the impact on fresh water in the U.S. comes from non-point sources, with population and land use playing an important role. Two major anthropogenic inputs to surface waters are chloride and sodium, derived mostly from urban contributions such as road salt. Additionally, nitrate represents another large input, primarily from agricultural sources such as fertilizers. Many water quality studies exist for rivers and streams in parts of the Northeastern U.S., which have yielded increases in chloride concentration over time. Concerns in central Ohio arising from road salt application and storage practices have developed in the past few years, including potential chemical effects on local wildlife in streams and road salt's role in polluting Ohio drinking water. Historical data on fresh water quality exist for many Ohio rivers but haven't been further utilized to observe ion concentration trends over past decades. Past data were tabulated from the United States Geological Survey and The Ohio State University School of Earth Sciences to identify long-term trends in ion concentrations in rivers at multiple locations throughout the greater Columbus and central Ohio area. In June 2012 and March 2013, a number of sites were sampled for major ions and nutrients and compared to previous data. Comparing the 2012-2013 samples to those from same sites in the past, identifiable trends showing general increases in ion concentration over time were found in the river locations with complete historical data sets. The time series of some localities are not complete due to many gaps in data collection over the past 40-50 years. Analysis of chloride to bromide mass ratios in the Ohio surface waters revealed that the source of chloride was likely halite, or road salt.

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Introduction

Many natural and anthropogenic factors affect the geochemistry of surface waters like rivers and streams in both rural and urban areas. Much of the impact on fresh water in the United States comes from non-point sources, like road runoff, with population and land use playing an important role in water quality. The salinization of fresh water occurs by means of surface runoff related to rural agricultural practices and increasing suburban and urban coverage of roadways. Major components of salt input into rivers and streams are sodium and chloride, derived mostly from modern urban contributions of halite, or road salt, whereas anthropogenic input of nitrate largely comes from agricultural sources such as fertilizers. The application of road salt lowers the freezing point of water and therefore snow and ice, but it creates brine that is susceptible to running off roadways. Consequently, this melted saltwater is very difficult to control and can travel a variety of pathways, diffusing into the surrounding rivers and streams and perhaps infiltrating into the ground. This results in a decrease in high-quality fresh water resources and drinking water supplies for humans, the degradation of roadside habitats, and the deterioration of aquatic ecosystems and life. Many terrestrial and aquatic ecological consequences arise from the salinization of freshwater, including the acidification of streams, alternation of mortality and reproduction in aquatic biota, and the mobilization of toxic metals due to ion exchange or impurities from pollutants (Kaushal et al., 2005). The long-term effects of these changes on human water resources and throughout aquatic ecosystems are not well understood, creating a future unknown ramification of increased salinization. In the latter part of the 20th century, modern agricultural advancements have resulted in the use of large amounts of manure, organic, and mineral fertilizers that leave high volumes of nutrients like nitrogen and phosphorus in soils that afterward end up in river systems (Kundzewicz et al., 2010). Road salt use in the Northern, Northeastern, Midwestern and Great Lakes Region of the United States and its impact on the quality of surface water and groundwater has been examined by the scientific community in recent years. Relevant U.S. studies addressed for this project include Kelly et al. (2012), Panno et al. (2006), Mason et al. (1999), Kaushal et al. (2005), and Chapra et al. (2009).

Issues in Central Ohio arising from road salt application and storage practices have manifested in the pages of The Columbus Dispatch in the past few years, targeting topics including the chemical effects on local wildlife in streams, road salt's role in polluting Ohio drinking water, and implications of EPA guidelines on salt storage practices. Ohio had an annual road salt application rate of 200 kg/ha in the 1990s, while the rate of salt usage for highway deicing has increased yearly by 2-3% since the late 1970's (Chapra et al., 2009). During the recent 2012-2013 winter season, The Ohio Department of Transportation used more than 720,000 tons of salt statewide clearing highways of snow and ice. In central Ohio alone, 66,000 tons of salt were used, with more than 20,000 tons used solely in the city of Columbus and 25,000 tons still in storage as of March 2013. ODOT spent around \$1.1 million on salt for Columbus and \$79 million statewide (Rouan, 2013; Trimble, 2013). This is almost double the amount of money spent and salt used compared to the previous year during a milder winter, however despite this fact, this year's salt use and spending is near the historical average (Rouan, 2013). The Ohio EPA found evidence in five Ohio communities of runoff from road salt storage piles contaminating public and private wells since 2009. Furthermore, wells had to be abandoned in Cambden, Preble County, OH, just West of Dayton, when the salty taste in drinking water could no longer be tolerated (Hunt, 2010). In central Ohio, drinking water concerns pertinent to storm water runoff from salt piles has recently lead the Ohio EPA to create

road salt storage guidelines for businesses and cities. Although these are not laws and have not been officially adopted yet, the guidelines request that road salt be stored outside of flood prone areas, a minimum of 300 feet from streams and wells, and at least 100 feet from ditches and storm drains. For salt piles more than 3,000 pounds, the Ohio EPA has maps that show areas of groundwater vulnerable to pollution (Hunt, 2012). The city of Columbus stores its road salt in six barns with concrete floors (Hunt, 2010).

Bromide, like chloride, acts conservatively in ionic form, thus representing a good indicator of geochemical source. Due to chemical similarities between the elements of chlorine and bromine, the concentration of bromide relative to chloride in water samples is used to determine the sources of chloride in natural water systems. Much previous research has utilized the study of bromide and chloride together to study the origins and transformation of salt waters in natural surface, subsurface, and groundwater systems. Studies that examine Cl/Br mass ratios of waters affected by the dissolution of halite include those of Davis et al. (1998, 2001) and Panno et al. (2006).

Goals and Objectives

Unlike most other regions in Ohio, the metropolitan Columbus area has seen population growth in the past two decades, resulting in ever expanding urbanization and suburban sprawl. Rather little is known about the relationship between urban and suburban development across the United States and its impact on long-term changes in baseline salinity of fresh surface water. Historical data on fresh water quality exist for many rivers and streams throughout Ohio, however much of it has never been utilized to observe such trends as chloride and nitrate flux through time. Due to chloride's conservative nature, low natural background levels, and ability to be measured with reasonable precision, it serves as an indicator of anthropogenic influence on water quality (Chapra et al., 2009). The overall goal of this research is to identify possible anthropogenic induced trends in chloride, sodium, or nitrate flux through time in a number of Ohio rivers that are located in areas of urban and suburban influence. Rivers studied include the Hocking River, Olentangy River, Little and Big Darby Creeks, Alum Creek, and Little Miami River. Since a single sample is hardly representative of all the water in a river, it alone cannot be used to genuinely detect contamination. Thus, the incorporation of historical data aids in developing a comprehensive picture of river development and condition. By measuring ion concentrations and isotopic values in these Ohio surface waters, similar characteristics between contributing factors are identified and compared with past water quality records. In order to resolve water contamination issues, it is necessary to identify the source of contamination. Therefore, another objective of this research is to determine the origin of chloride found in the surface waters. Analysis using Cl/Br mass ratios is utilized to aid in the interpretation of chloride sources. Specifically, the application of road salt, or halite, is investigated as the main source of chloride input for surface waters throughout Ohio.

Methodology

I have tabulated past data from federal sources such as the U.S. Geological Survey National Water Information System (NWIS) and data from Dr. Berry Lyon's and Dr. Anne Carey's research groups from the 2000's to identify long-term trends in ion concentrations in rivers at multiple locations throughout the greater Columbus area. On June 19 and 21, 2012 and March 2, 2013, the same sites examined in the past by USGS workers were sampled, or in some cases nearby sites due to limited access beneath roadways and bridges or due to steep slopes. A total of 14 sample locations were studied at various locations of the Olentangy River, Little and Big Darby Creeks, Hocking River, Little Miami River, and Alum Creek (see Figure 1):

OA: Olentangy River, Drake Union, The Ohio State University; merged with past data from Dr. Lyon's research group and USGS site no. 3226885 at Henderson Rd

OC: Olentangy River, Worthington, Olentangy Trail at OH-315N and I-270E; merged with past data from Dr. Lyon's research group at Highbanks Metro Park and USGS site no. 3226800

OD: Olentangy River, Delaware, County Rd 213/Main Rd off US-23N; merged with past data from USGS site no. 3225500

OE: Olentangy River, Claridon, River Bend Campground, Whetstone River Rd; merged with past data from USGS site no. 3223000

DC: Little Darby Creek, West Jefferson, near McDonalds parking lot on E. Main St; merged with past data from Dr. Carey's research group and USGS site no. 3230310

DD: Big Darby Creek, Darbydale, Harrisburg Georgesville Rd near Osprey Lake; merged with past data from Dr. Carey's research group and USGS site no. 3230400

DE: Big Darby Creek, Darbyville, OH-316E just East of downtown Darbyville; merged with past data from USGS site no. 3230500

DF: Big Darby Creek, Plain City, OH-161 at Butler Ave/County Highway 3; merged with past data from USGS site no. 3230200

HA: Hocking River, Logan, South of US-33 on State Route 93 at Kachelmacher Park

HB: Hocking River, Lancaster, Canal St at S. Columbus St; merged with past data from USGS site no. 3156400

HC: Hocking River, Enterprise (near Logan), Zeller Rd; merged with past data from USGS site no. 3157500

HD: Hocking River, Athens, Stimson Ave near US-33; merged with past data from USGS site no. 3159500

LB: Little Miami River, Yellow Springs, US-68S near Clifton Rd; merged with past data from USGS site no. 3240000

AE: Alum Creek, Kilbourne, County Rd 34/N Galena Rd; merged with past data from USGS site no. 3228750

At each sample location, an individual wearing vinyl gloves took two samples, one with a precleaned 125mL wide mouth low-density polyethylene (LDPE) bottle and one with a 20mL plastic scintillation vial with a poly cone cap. Before filling each bottle, water from the stream was used to rinse the bottles. Then, the open container was pointed into the flow of the stream to collect the sample. The 125mL sample at each location was for cation and anion analysis via ion chromatography and nutrient analysis via a Skalar Autoanalyzer. The 20 mL sample was for H₂O isotopic analysis via cavity ringdown spectroscopy. The samples for ion and nutrient analysis were filtered either on-site or shortly after at the lab located on The Ohio State University Campus. Samples were filtered through Whatman 0.45um polypropylene filters using a plastic disposable filtering device. Until analyses were completed, samples were kept cool and in the dark. Not every site sampled in June 2012 was sampled again in March 2013 either due to difficulties in reaching the water because of ice and snow or due to a lack of long-term consistent historical data for the sample site.

To ensure the data from ion chromatography could be taken as a primary signal of water quality, analysis of deuterium and oxygen-18 isotopes in the water samples were compared to local rainwater precipitation samples obtained from Deb Leslie of The Ohio State University from her research on Ohio precipitation geochemistry. Isotopic values from both the river and rainwater samples were plotted with the Global Meteoric Water Line (GMWL) to determine if evaporation should be considered as a factor affecting the June 2012 ion data (Craig, 1961).

Results

Deuterium and oxygen-18 isotopic values from the June 2012 river samples are plotted with Central Ohio precipitation samples and the Global Meteoric Water Line (Craig, 1961) in Figure 2. All cation, anion and nutrient data for the June 2012 and Winter 2013 river samples from central Ohio are reported in Tables 1 and 2. In the rest of this text, I will refer to these samples as the “2012-2013” samples. Nitrate data is presented as N-NO₃, or nitrate as nitrogen. Precision of the measurements is demonstrated in Table 3 as the percent difference between duplicate measurements.

The range of chloride concentrations for June 2012 was 18.7-79.3 mg/L, LB and OC respectively, with a mean of 46.6 mg/L and a median of 47.1 mg/L. The range of sodium concentrations for June 2012 was 8.0-46.8 mg/L, LB and OC respectively, with a mean of 27.3 mg/L and a median of 27.1 mg/L. The range of nitrate concentrations for June 2012 was 0.5-7.90 mg/L, OA and AE respectively, with a mean of 1.8 mg/L and a median of 1.1 mg/L.

The range of chloride concentrations for March 2013 was 33.1-71.9 mg/L, HD and OC respectively, with a mean of 54.0 mg/L and a median of 58.0 mg/L. The range of sodium concentrations for March 2013 was 15.6-39.0 mg/L, DC and HB respectively, with a mean of 27.4 mg/L and a median of 28.9 mg/L. The range of nitrate concentrations for March 2013 was 1.68-9.33 mg/L, HD and DC respectively, with a mean of 5.3 mg/L and a median of 4.3 mg/L.

For the seven sites sampled in both June 2012 and March 2013, Table 4 shows the percentage change in chloride, sodium, and nitrate concentration. Table 5 presents downstream profiles of the June 2012, March 2013, and historical averages of chloride, sodium, and nitrate concentrations for sample locations on the Olentangy River and Darby Creek. Dashed spaces indicate either a lack of historical data for the site or that no sample was taken.

Ion Chromatography was used to analyze the bromide concentration of each river sample. Chloride, bromide, and Cl/Br mass ratios from the June 2012 and March 2013 samples are listed in Table 6. The range of Cl/Br mass ratios for June 2012 was 600-5400, with a mean of 2500 and a median of 1900. The range of Cl/Br mass ratios for March 2013 was 830-9600, with a mean of 5300 and a median of 5200.

Time series showing chloride, sodium, and nitrate concentrations from the river locations with the most complete historical data sets are shown in Appendix A. A general timeline of sample dates is provided on the x-axis of each graph. For those graphs with many data points, sample dates have been periodically left out on the axis due to limited space. The majority of historical data provided by the USGS NWIS is from the 1950's, 60's, and 70's, whereas historical data from The Ohio State University School of Earth Sciences is mostly from the 2000's. Therefore, gray markers have been placed on the x-axis to indicate gaps in time where no data are provided. Time series of ion concentrations at the Olentangy River locations are shown in Figures 3 a-d; Darby Creek locations are shown in Figures 4 a-f; Hocking River locations are shown in Figures 5 a-b; and Little Miami locations are shown in Figures 6 a-c.

Discussion

Isotope Analysis

In 1961, Craig published his Global Meteoric Water Line that demonstrates the correlation between oxygen-18 and deuterium isotopes. The line is an approximation of isotopic enrichments in natural meteoric waters, i.e. those derived from the atmosphere, from all over the world relative to “standard mean ocean water” (SMOW). The isotopic values exhibit a linear relationship over the entire range of global waters that have not undergone excessive evaporation (Craig, 1961). Since publication, Craig's GMWL has been greatly utilized in the understanding of the hydrologic cycle. Generally, cold regions have low oxygen-18 values while warm regions have high oxygen-18 values. Surface waters that have undergone copious evaporation will exhibit oxygen-18 and deuterium values that deviate from the GMWL. Such waters are known to still show a linear relationship, however it generally has a gentler slope and extends outward from the right side of the GMWL. Due to the humid summer climate of Ohio, it is valuable to compare isotopic measurements of surface water samples taken during summer months to the GMWL to determine if evaporation should be considered as a factor affecting subsequent analyses and measurements. Figure 2 shows the GMWL plotted with the oxygen-18 and deuterium values of the June 2012 river samples and central Ohio precipitation samples provided by Deb Leslie of The Ohio State University. The scales of the y-axis and x-axis have been adjusted to provide a closer look at the position of the Ohio samples (for a full scale plot of the GMWL, see Craig, 1961). The purpose of including precipitation samples was to represent the isotopic characteristics of central Ohio meteoric waters for comparison with the river samples. In Figure 2, it is apparent that the June 2012 river samples are comparable to the precipitation samples and exhibit a linear trend similar to the GMWL. Additionally, they reveal no strong characteristics of waters affected by excessive evaporation. Thus, the ion concentrations of the June 2012 samples obtained via ion chromatography can be taken as a primary signal of water quality.

Road Salt in the Northeastern U.S.

After World War II, large-scale implementation of road salt use began and increased quickly post 1960's, resulting ever since in increasing Cl^- concentrations in groundwater and surface waters in urban areas of the northern U.S. (Kelly et al., 2012). Although elevated levels of Na^+ and Cl^- are becoming more common in surface and ground waters in northern regions of the U.S., road salt is currently not regulated as a primary contaminant to fresh waters (Panno et al., 2006; Kaushal et al., 2005). Additionally, the U.S. EPA has only a secondary standard of 250 mg/L for Cl^- in drinking water to account for salty taste and a recommended chronic criterion of 230 mg/L Cl^- for at least four days in surface waters for aquatic life (Panno et al., 2006; Kelly, et al. 2012). On the other hand, no limit for sodium even exists, but sodium levels above 20 mg/L in drinking water can be problematic to those with hypertension (Kelly et al., 2012). Thus, surface waters that are exposed to abundant halite dissolution may present a different type of pollution not particularly covered by environmental policies and regulations. Some researchers predict that if increases in salinity continue at the rate of today, many surface waters in the Northeastern United States will become toxic to freshwater life and will not be safe for human ingestion within the next century (Kaushal et al., 2005). In 2009, researchers at the University of Minnesota discovered increases in salt concentrations related to road salt purchases over a 22-year period in 39 Minneapolis-St. Paul lakes. Although Ohio agencies have not studied the toxicity of materials such as road salt to wildlife, the Minnesota study listed road salt as a threat to a variety of wildlife such as fish and frogs (Hunt, 2013). Researchers at Ashland University north of Columbus recently began a study related to the effects of salt on wildlife in rivers and streams.

In the Northeastern U.S., chloride additions via deicing salt have been abundant enough in the winter months to remain extremely high during the summers and throughout the rest of the year (Kaushal et al., 2005). A study was conducted by Kaushal et al. (2005) examining the rate of salinization of rural streams in three locations of the Northeastern U.S. including Baltimore County, Maryland, the Hudson River Valley, New York, and the White Mountains in New Hampshire. Despite the low-density of roadways in these areas, some rural stream chloride concentrations exceeded 100 mg/L throughout the year, suggesting changes in baseline salinity of surface waters and the prevalence of chloride contamination across geographic areas. A portion of the 2005 study also examined the Baltimore Metropolitan area, where chloride concentrations peaked in the winters during 1998-2003, reaching thousands of mg/L. Salinity in aquifers and groundwater in the Northeastern U.S. has also increased across all seasons from to the accumulation of road salt. Due to the conservative nature of chloride, it is predicted that even if salt use is stopped, elevated salinity can remain in groundwater systems for decades. Kaushal et al. (2005) declared, "salinization associated with increasing suburban and urbanization deserves attention as one of the most significant threats to the integrity of freshwater ecosystems in the Northeastern United States" (p. 13519). Panno et al. (2006) and Kelly et al. (2012) monitored surface waters near the Chicago, IL region and observed notable increases in both Cl^- and Na^+ since the mid 1970's, with the most accelerated increases observed in areas of rapidly changing rural to urban land use.

Increased chloride concentrations have also been reported in the Laurentian Great Lakes of the U.S. Historical data collected from numerous sources by Chapra et al. (2009) indicates that in the first six decades of the 20th century, chloride exponentially increased in all the Great Lakes, excluding Lake Superior. These lakes also all showed peak chloride concentrations

around 1965-1975, with reduced levels in subsequent years, while current trends demonstrate that chloride is rising again. Lake Erie Cl^- concentration peaked at around 26 mg/L and decreased gradually to about 14.5 mg/L by 1988, rising steadily each year to levels above 18 mg/L in 2009 (Chapra et al., 2009). Pre-1960's increased chloride concentrations are mostly due to industrial discharges from large production areas located near the Great Lakes, including Cleveland and Detroit. Starting in the late 1960's and continuing over the past 35 years, there have been major reductions in industrial discharges from this area, likely representing the observed decreases in lake chloride concentrations during the 1970's. However, the recent increasing trends of chloride suggest input from other sources, such as increased road salt use in the watersheds near the lakes and possibly new industrial sources (Chapra et al., 2009). Comparing past industrial inputs to road salt use today, it is apparent that current influences could be more diffuse and prove more difficult to control in the near future.

Chloride and Sodium

Panno et al. (2006) considers chloride concentrations in the range of 50 to 1000's of mg/L are present in water samples affected by road salt and that background concentrations in shallow aquifers in northeastern Illinois range from <1 to 15 mg/l for both Na^+ and Cl^- . Chloride concentrations from 2012-2013 listed in Tables 1 and 2 are mostly near or in the bottom part of the 50+ mg/L range. Assuming the background concentrations in IL hold relatively true for central Ohio natural waters, every Cl^- & Na^+ concentration of March 2013 samples and all but four Na^+ concentrations of June 2012 samples are above 15 mg/L, indicating the artificial addition of chemical inputs to Ohio rivers, likely derived from human activity. Table 4 reveals higher chloride and sodium concentrations for March 2013 at many locations, probably due to the stark differences between the 2011-2012 and 2012-2013 road salt use totals discussed previously in the Introduction (See Rouan, 2013). Lower Cl^- and Na^+ concentrations observed at some locations in June 2012 relative to March 2013 could be related to the much milder winter that preceded the summer of 2012. Either increases in both chloride and sodium or decreases in both ions are observed between June 2012 and March 2013 at all sites besides HB (See Table 4). This trend is what to be expected in surface waters if halite is the main source of Na^+ and Cl^- to the system (Kelly et al., 2012). Higher winter chloride and sodium concentrations have been reported in other studies. Kaushal et al. (2005) had the highest chloride concentrations in streams of urban areas in Baltimore during winter from 1998-2003. Kelly et al. (2012) also reported higher Na^+ and Cl^- concentrations in winter in the Chicago, IL area, likely as a result of direct runoff from salted roads, with the lowest concentrations of both ions between July and October and highest in February, March and January, respectively.

Stucker et al. (2010) reported chloride concentrations of Olentangy River tributaries that represent the lowest order streams ranging from 1675-4400 μM , or around 58-154 mg/L. Additionally, chloride concentrations for rivers in the Chicago Metropolitan area were mostly above 100 mg/L from 2001-2005 and have been increasing with time. Although June 2012 and March 2013 chloride are not above 80 mg/l, the time series of many sample locations show general increases in Cl^- concentration over time. Figure 4c of Big Darby Creek at Darbydale (DD) shows an increase in average Cl^- from the 1960's to 2007, with both 2012 and 2013 samples above the 2007 average. The site with the longest set of historical data is the Hocking River at Athens (HD), dating back to 1955, which shows a characteristic increase in chloride beginning in the early 1960's (See Figure 5a). This reflects the beginning of large-scale road salt

application post World War II, supporting the argument that halite dissolution has impacted the river. Yet, the Athens site showed the largest decrease of any site in chloride and sodium concentrations from June 2012 to March 2013 demonstrated in Table 4, reflecting the variability of the time series trendline rather than the yearly historical averages. Figure 6b shows the time series for the Little Miami River at Milford in west central Ohio. Even though this site was not sampled during June 2012 or March 2013, it has one of the most complete datasets through the 80's and 90's and demonstrates increased chloride concentration over the last half of the 20th century. The 2000's average is slightly lower than the 1990's, but this could be a result of fewer data points provided for the decade. Time series of chloride trends in other Ohio rivers reveal no strong trends in increase of chloride over time, but still exhibit June 2012 or March 2013 Cl^- concentrations higher than the historical average. Figure 3a shows June 2012 chloride for the Olentangy River at site OE as nearly 10 mg/L higher than the average in the 1960's and 70's. Due to the close proximity and similarities in human activity at the Worthington and Drake Union sites on the Olentangy (OA and OC), their historical chloride concentrations were combined and are shown in Figure 3b. Although no clear increasing trend can be distinguished in the trendline, all four samples from 2012 and 2013 are above the historical average of the 60's, 70's, and 2000's. Two more Darby Creek locations, DC and DE, show no characteristic increasing trend through time. Figure 4e shows that both 2012 and 2013 samples for DE were above the historical average for chloride at that location, however Figure 4a of DC contains more historical data from recent decades and shows that only the March 2013 sample was higher in Cl^- than historical average. Chloride and sodium concentrations from river to river show no strong pattern, however the highest concentrations for both ions occur in sites on the Olentangy and Hocking Rivers. Chloride trends in rivers with the most complete historical datasets are either increasing or random, with no decreasing trends observed at any of the river locations. These observations suggest that chloride is likely on the rise throughout Ohio as a whole, while previous research advocates increasing chloride across the geographic region of the Northeastern United States.

Examination of downstream trends in ion concentration suggests that local factors like land use are possibly impacting the rivers. Downstream profiles of ion concentration in Table 5 reveal that both June 2012 and March 2013 samples for Darby Creek locations are higher at the two locations south of the city of Columbus, perhaps indicating the impact of runoff on downstream water quality. However, historical data for Darby Creek sodium levels are lacking, whereas the historical average of chloride shows no real trend downstream. For the Olentangy River, chloride and sodium during 2012 and 2013 decrease at OD going south, then increase dramatically at site OC before decreasing slightly again at OA. These trends differ from the historical average downstream profiles, where chloride increases gradually downstream from OE to OA and sodium is relatively unchanged at all sites besides OC. Generally, higher Cl^- and Na^+ concentrations in the Olentangy River are observed at the southernmost sites OC and OA. Jacobs (2006) reported Olentangy River ion concentrations from 2004-2006 at two locations, one in central Franklin County and one just north of Franklin in Delaware County, of 0.437-2.56 mM Cl^- and 0.291-2.26 mM Cl^- , respectively. These ranges are the equivalent of 15.3-89.6 mg/L and 10.2-79.1 mg/L. Sodium values for the Franklin County and Delaware County sites were 0.362-2.08 mM Na^+ and 0.259-1.79 mM Na^+ respectively, with equivalent ranges 8.3-47.8 mg/L and 5.9-41.2 mg/L. Higher concentrations in Franklin County relative to Delaware also suggest higher chloride concentrations downstream in the Olentangy, which could reflect increased road salt application near the more urban areas of the watershed (Jacobs, 2006). On the contrary,

Heffelfinger (1995) observed decreasing concentrations of sodium downstream in the Olentangy during August 1995 from a site north of Delaware to one just south of Columbus, attributing the decrease to increased discharge of the river with little addition of sodium. This observation correlates more with the historical average downstream profile at Olentangy sites, where OC has a concentration of 38.8 mg/L Na^+ and the historical concentration of OA to the south is only 18.5 mg/L Na^+ . However, when comparing trends in chloride to those of sodium in natural water systems, an understanding of their geochemical differences is crucial. Water affected by road salt usually has excess Cl^- compared to Na^+ , despite the fact that equimolar concentrations of both ions are present in unimpacted surface waters. Unlike conservative chloride ions, Na^+ takes part in cation exchange reactions and thus is more likely to be retained in the subsurface (Kelly et al., 2012). For example, road salt derived sodium displaces Ca, Mg, and K from soil, increasing their concentrations in surrounding waters. Eventually, the exchange process reaches a steady state where additional Na^+ moves more conservatively through soil and Ca, Mg and K return to previous values, however it should be known that sodium concentrations may not reflect all the sodium present in natural water systems due to these processes (Mason et al., 1999). In all the June 2012 and March 2013 samples, Na^+ concentrations are lower compared to Cl^- , which could reflect either the participation of Na^+ in ion exchange processes or the additional presence of CaCl_2 as an impurity in road salt relative to NaCl (Jacobs, 2006). The time series of sodium concentration at Athens (Figure 5b) does not show the same gradual increase in concentration as chloride at Athens; however, it is beneficial to note the periodicity of the historical trend. The recurring increases in sodium through the 50's and 60's are characteristic of higher concentrations during the months from October to December, different from Kelly et al, (2012) who observed the lowest concentrations in IL through October and the highest in February, demonstrating the increased complexities of studying sodium concentration over time. Eastin (1970) sampled the Olentangy River near The Ohio State University Campus in 1966 and measured sodium concentrations in the range of 17-39 mg/L with an average of 22.3 mg/L. This value correlates with the historical average of the Olentangy at OC (Figure 3d), while both 2012 and 2013 values are well above 22.3 mg/L. The Olentangy River at Drake Union (OA) had June 2012 and March 2013 concentrations of 36.9 mg/L and 29.1 mg/L of Na^+ , respectively and is located closest to where Eastin sampled in 1966. Additionally, Heffelfinger (1995) reported a range of 4.44-29.2 mg/L Na^+ with an average of only 9.7 mg/L for sites along the Olentangy River, lower compared to the majority of sodium concentrations of 2012 and 2013 samples. These observations may suggest that sodium has been increasing through time in the Olentangy River, but overall, identifying historical trends for sodium in Ohio rivers was more difficult because there is the least amount of recorded data for this ion.

Nitrate

Historical data for nitrate does not differ dramatically with June 2012 concentrations at most sample locations. In fact, Figures 3c, 4b, 4d, and 4f of OA and OC combined, DC, DD, and DE respectively, demonstrate that the June 2012 nitrate concentration was below historical averages, suggesting a possible decrease of nitrate in recent years. Since public awareness of nitrate contamination in freshwaters began around the 1980's, Sprague et al. (2011) has examined if any progress had been made in reducing riverine nitrate in the Mississippi and its tributaries, including the Ohio River. The study reveals that in the Mississippi Basin, little progress has been made in recent decades, with indication of increased nitrate flux and concentrations in some parts.

Despite the low June 2012 concentrations, all locations that were re-sampled in March 2013 displayed a nitrate increase of at least 70% and all are above historical averages (See Table 4). Jacobs (2006) also observed that nitrate concentration in the Olentangy River in 2006 varied greater than that of chloride, with the lowest concentrations in June, a similar characteristic in this study. Higher nitrate concentrations in winter are possibly due to the leaching of fertilizers and manure from agricultural lands from increased snowfall and precipitation. Jacobs (2006) reported 2004-2006 Olentangy River nitrate concentrations at a site in Franklin County and one just north in Delaware County of 0.068-0.309 mM and 0.018-0.339 mM, respectively. These ranges are the equivalent of 4.2-19.1 mg/L and 1.1-21.0 mg/L. Unlike sodium and chloride, Jacobs' nitrate concentrations showed less evidence of increase downstream in the Olentangy (2006). The nitrate downstream profile of Olentangy River sample sites in Table 5 reveals similar characteristics to Jacobs, with no significant trend of nitrate flux throughout the river. For the locations along Darby Creek, the historical average for nitrate concentrations may indicate an increase in concentration downstream, with a change in nitrate from 0.7 mg/L N-NO₃ at DF to 2.8 mg/L N-NO₃ at DE. However, values for the 2012 and 2013 sample dates show no downstream trends.

Cl/Br Analysis

Chlorine and bromine are present in natural water systems commonly as the monovalent anions Cl⁻ and Br⁻. Although many factors can affect the chloride/bromide ratios in settings, the movement of both ions is commonly conservative (Davis et al., 1998). Since both Br⁻ and Cl⁻ act conservatively when dissolved in water, are both small in ionic size, neither take part in low-temperature ion exchange reactions, and neither occurs in common rock-forming minerals in large concentrations apart from evaporite minerals, their natural relationship provides geochemical information that is both complementary and routinely overlapping (Davis et al., 1998). The main difference between chloride and bromide is due to their abundances in natural solids and fluids, where chloride is commonly 40-8000 times more abundant than bromide. As a result, a very small change in bromide concentration with no change in chloride will have a large impact on the Cl/Br mass ratio (Davis et al., 1998). The most important geochemical difference to note between chloride and bromide deals with solubility. Compounds of bromide are known to be even more soluble than compounds of chloride, so when extreme evaporation permits the precipitation of halite, the resulting brine is left enriched in bromide (Davis et al., 339, 1998). Consequently, the halite has a very low bromide concentration compared to chloride, resulting in very large mass ratios of Cl/Br in the material. Halite is the main deicing material used to salt the roads in regions like the Northeastern U.S., so surface waters impacted by road runoff during the winters are likely to be affected by the dissolution of halite. Since halite contains essentially no bromide, the addition of chloride from road runoff to surface waters results in very large Cl/Br mass ratios. Generally, coastal areas exhibit Cl/Br natural mass ratios near 250 that vary to around 50 in north central states, with anything above 300 attributed to sources of chloride other than atmospheric deposition (Davis, et al., 2001). Davis et al. (1998) determined that the Cl/Br mass ratios for waters affected by the dissolution of halite are generally in the range of 1000-10,000, compared to the seawater ratio of 290. Panno et al. (2006) determined that groundwater samples affected by road salt from northeastern Illinois had Cl/Br ratios of 1164-4225. The Cl/Br mass ratios from the majority of June 2012 and March 2013 river samples in Table 6 were in the 1000-10,000 Cl/Br mass ratio range for waters affected by halite dissolution determined by

Davis et al. (1998). Only 4/14 samples from 2012 and 2013 were outside the range, however they all were greater than 600 and thus well above any natural mass ratios of surface waters (See Table 6). June 2012 and March 2013 mean mass ratios of 2500 and 5300 and median mass ratios of 1900 and 5200, respectively, suggest the rivers have been affected by halite dissolution.

In their 2001 study, Davis et al. measured Cl/Br mass ratios in 21 samples of spring water from 10 states. Analysis of spring water from Big Spring, Iowa revealed a chloride concentration of 24.7 mg/L and a Cl/Br mass ratio of 948, the highest in the study. Although bromide data are not provided, the mass ratio suggests a concentration around 0.026 mg/L Br⁻. The ratio alone reveals that a large amount of Cl⁻ was introduced into the system by means other than natural deposition. Suggested artificial sources of chloride included either road salt or agricultural sources like fertilizer and animal waste (Davis et al., 2001). Nitrate analysis of the Big Spring sample revealed a concentration of 56 mg/L, or an equivalent of 12.6 mg/L N-NO₃, the largest in the study by far, thus favoring the agricultural source for the Cl⁻. The spring water concentrations of 0.026 mg/L Br⁻ and 24.7 mg/L Cl⁻ from Iowa in comparison to the concentrations of Ohio rivers in this study are very similar. Average bromide concentration for the 2012 and 2013 samples are 0.032 mg/L and 0.017 mg/L respectively, while average chloride concentrations are 46.6 mg/L and 54.0 mg/L respectively. Although the Cl⁻ is higher in the Ohio samples, the nitrate concentrations are lower than the 12.6 mg/L N-NO₃ reported for the Big Spring water with a 2012 average of 1.83 mg/l and a 2013 average of 5.26 mg/L. Since nitrate concentrations in central Ohio samples are probably too low to indicate major agricultural contributions of chloride, and the Cl/Br mass ratios and respective Cl⁻ and Br⁻ concentrations of the Iowa spring water and the Ohio samples are similar, chloride derived from road salt is the likely source of Cl⁻ in the Ohio rivers. Nonetheless, the higher Cl/Br mass ratios seen in March 2013 accompanied by notable increases nitrate concentrations at every site suggests the leaching of fertilizers from agricultural lands during the winter season could have played a role in contributing chloride to the rivers.

The Cl/Br mass ratios of March 2013 samples by location are all higher than those of June 2012 (See Table 6). Bromide concentrations of June 2012 are slightly higher than those of March 2013 at the same location, while chloride concentrations between sampling dates increased at most sites but decreased at others. In locations such as OA, there is a 10 mg/L decrease in chloride concentration in March 2013 and a 180% decrease in bromide concentration relative to June 2012, yet the Cl/Br mass ratio is more than twice as large as June 2012. Conversely, locations such as HB had no extreme changes in Br⁻ concentration and a 16 mg/L increase in Cl⁻ concentration in March 2013, resulting in a higher Cl/Br mass ratio. Therefore, the slight decreases in bromide concentration at each location, either accompanied by an increase in chloride concentration or not, resulted in the higher Cl/Br mass ratios of March 2013 relative to June 2012.

Conclusions

The major conclusions of this study are:

- Identifiable trends were found in river locations with complete historical data sets, showing general increases in Cl^- concentration over time beginning in the 1960s. Chloride and sodium for other rivers exhibit no real trend through time but still demonstrated 2012-2013 concentrations higher than historical averages. The time series of some localities are not complete due to many gaps in data collection over the past 40-50 years.
- Either increases in both chloride and sodium or decreases in both ions are observed between June 2012 and March 2013 at all sites besides the Hocking River at Lancaster, OH. This is the expected trend in waters where halite is the main source of Na^+ and Cl^- . For the most part, higher chloride and sodium concentrations were observed in winter, similar to other studies that examined chloride and sodium trends in the Northeastern U.S.
- Chloride concentration trends for all rivers were either increasing or random, with no decreasing trends observed, suggesting that chloride is likely on the rise throughout regional Ohio. Previous similar research supports increasing chloride across the geographic region of the Northeastern United States.
- Na^+ concentrations in 2012-2013 central Ohio samples are all lower than respective Cl^- concentrations, possibly reflecting the participation of Na^+ in ion exchange reactions or the presence of CaCl_2 as an impurity in road salt relative to NaCl . Identifying trends in sodium levels over time was more difficult due to the lack of historical data for this ion.
- The downstream profile of historical averages for chloride concentration at Olentangy River sites displays an increasing trend, possibly reflecting increased road salt application near the more urban areas of the watershed.
- Historical data for nitrate do not differ dramatically from June 2012 concentrations at most sample locations, however March 2013 concentrations showed increases of at least 70% relative to 2012 levels, possibly due to the leaching of fertilizers and manure from agricultural lands from increased snowfall and precipitation.
- Mean and median values for Cl/Br mass ratios for June 2012 and March 2013 samples were between the 1000-10,000 Cl/Br range expected for waters affected by halite input, suggesting the origin of Cl^- in these waters is in part from road salt.
- Observations of the select Ohio rivers in this study are similar to what have been observed elsewhere in the U.S., but others show no real trends. A lack of consistent long-term data leads to a lack of certainty in interpretation of the time series at some locations.

Recommendations for Future Work

Further research investigating the sources of chloride in surface waters will shed light upon how urban and suburban development in Ohio has influenced the changes of baseline salinity in fresh water over time. In addition to Cl/Br mass ratios, the analysis of the radionuclide chlorine-36 has been utilized to aid in the interpretation of chloride sources. Chlorine-36 is produced in the upper atmosphere by cosmic-ray spallation and has a long half-life of over 301,000 years. More recently, chlorine-36 was released into the atmosphere in very large amounts from 1950's nuclear weapons testing in the Pacific, establishing it as a useful hydrologic tracer worldwide (Davis et al., 2001). The ocean is generally considered to have essentially no chlorine-36, with ratios of $^{36}\text{Cl}/\text{Cl}^{\text{total}}$ increasing near the center of continents. Consequently, halite taken from deposits formed by the evaporation of saline or seawater long ago for utilization as road salt has essentially no ^{36}Cl . Therefore, by analyzing river samples for chlorine-36, the presence or lack of chlorine-36 reveals information about the source of chloride in water. Summer 2012 samples from the Olentangy River and Darby Creek have been sent to Purdue University's National Science Foundation funded Rare Isotope Measurement Laboratory (PRIME Lab) in West Lafayette, Indiana, where they are waiting to be analyzed using accelerator mass spectrometry. These results will provide a better understanding of road salts impact on the central Ohio rivers.

In terms of road salt and the environmental impact on surface, subsurface, and ground waters alike, better storage management and better application techniques at the local level should be created to minimize unnecessary salt application. Since the lack of long-term data for many Ohio rivers affected the analysis of this study, it is key that urban water quality monitoring in the Northern and Northeastern U.S. is maintained in the future. The continuance of studies regarding road salt's effect on wildlife, such as a recent one at Ashland University (Hunt, 2013), will expand both scientific knowledge and public awareness of road salt's negative environmental impacts and provide a more holistic understanding of the geochemical characteristics of halite dissolution in surface waters.

Climate change mitigation efforts in regards to surface freshwater quality will rely on the specific hydrology and meteorology of a region. Overall, a water system's response to climatic and non-climatic influences will rely on the types of water bodies present and the resource management area (Murdoch et al., 2000). Therefore, in order to develop mitigation strategies and techniques, each area must be individually monitored over time to determine the trends, characteristics, and thresholds of a system. However, due to the multi-factor context of water quality analysis, there will almost always be uncertainty associated with water quality modeling and results should never be taken as exact values but instead as indicators of possible trends (Kundzewicz et al., 2010). Currently, only a small number of monitoring programs for water quality exist, creating the need for "a baseline-monitoring infrastructure for tracking trends in discharge, temperature, and chemistry" to be established and retained (Murdoch et al., 2000). Obstacles in modeling techniques still remain because many of them only evaluate one or two variables of an ecosystem. In order to simulate the responses of whole water systems, models will need to demonstrate the biogeochemical relationships between climate, soil, land use, streams, rivers and lakes collectively. Monitoring and mitigation development go hand in hand and rely on the collection and utilization proxy data.

Of all Earth's accessible freshwater that is transferred from land to ocean, one third is currently used for human needs (Murdoch et al., 2000). In correlation with population growth seen in today's world, water pollution is also on the rise. Due to the similarities between the climate system and the freshwater resource system, they are closely linked and often induce changes in one another. Water quality is influenced by climatic factors such as temperature, occurrence of extreme weather events, and precipitation. Air temperature increase causes an increase in water temperature. This warming results in an increase in chemical reaction rate, accelerating nutrient cycling, and results in decreased oxygen carrying capacity that subsequently depletes oxygen concentration. Streams with less oxygen are not able to "self-purify" as efficiently, leading to less sustainable healthy water systems (Kundzewicz et al., 2010). In some areas, changes in water and land use could be either a response to or cause of climate change, such as through responding to demographic shifts or altered irrigation practices, or leading to the clearing of forests and desertification. In turn, changes in resource use could either worsen or mitigate water quality changes resulting from climatic variability (Murdoch et al., 2000). This possibility along with the difficulties that arise from the multi-factor context of water quality demonstrates the current inadequate understanding of the connections between climate change and water quality.

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Appendix A

Figures

Figure 1. June 2012 and March 2013 sample locations.

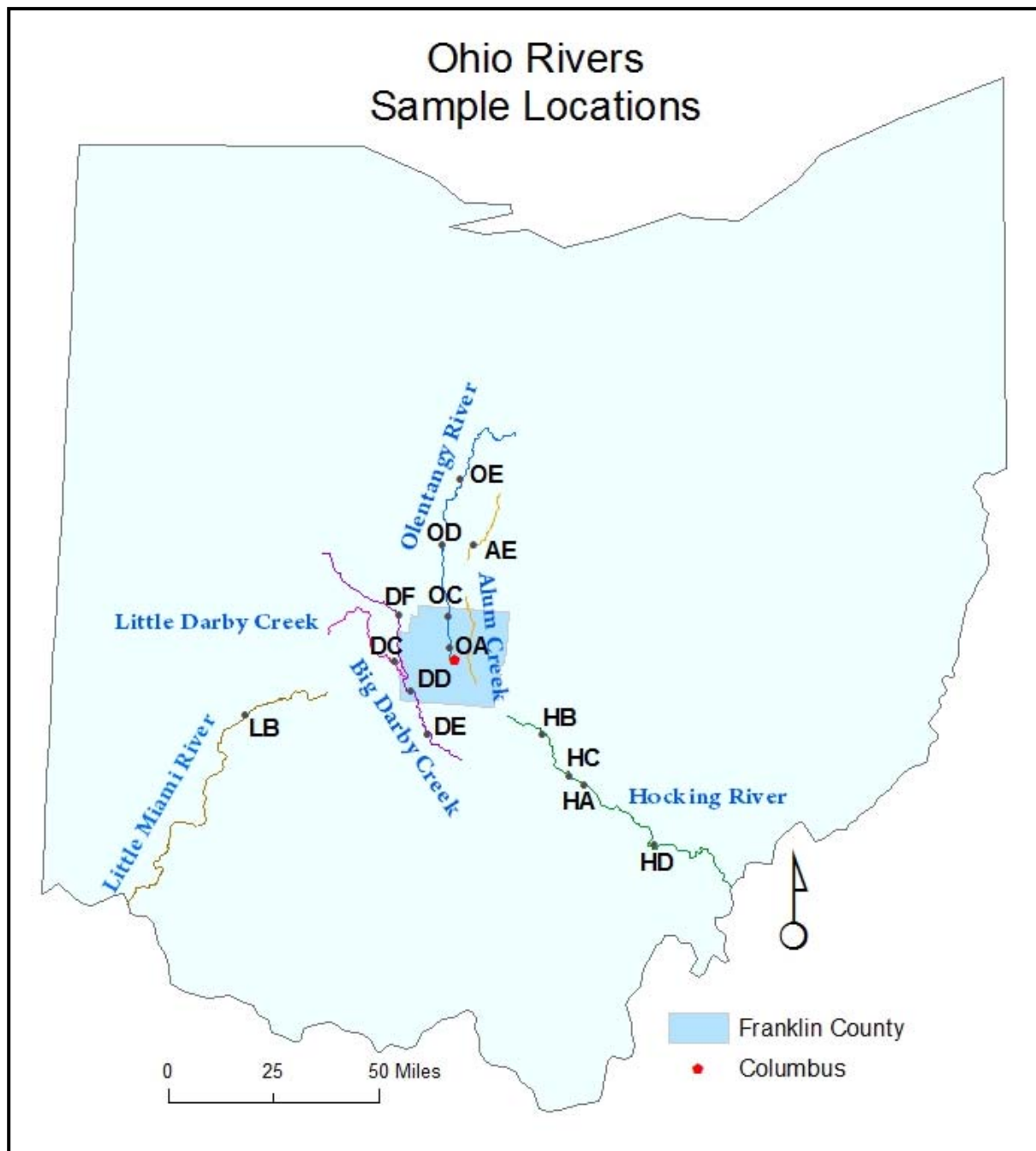


Figure 2. Global Meteoric Water Line (Craig, 1961) with Central Ohio Precipitation Samples (D. Leslie) and June 2012 Ohio river samples.

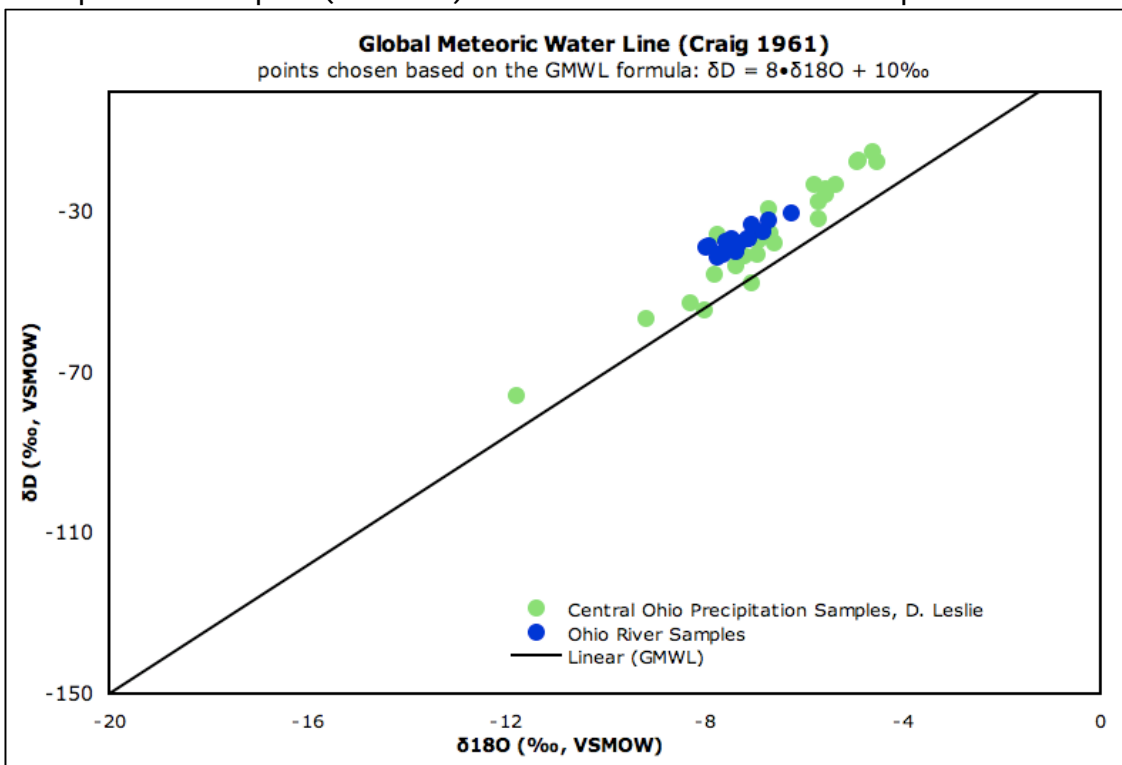


Figure 3a. Time series of chloride concentration at Olentangy River, Claridon OH. Historical Data from USGS NWIS site no. 3223000.

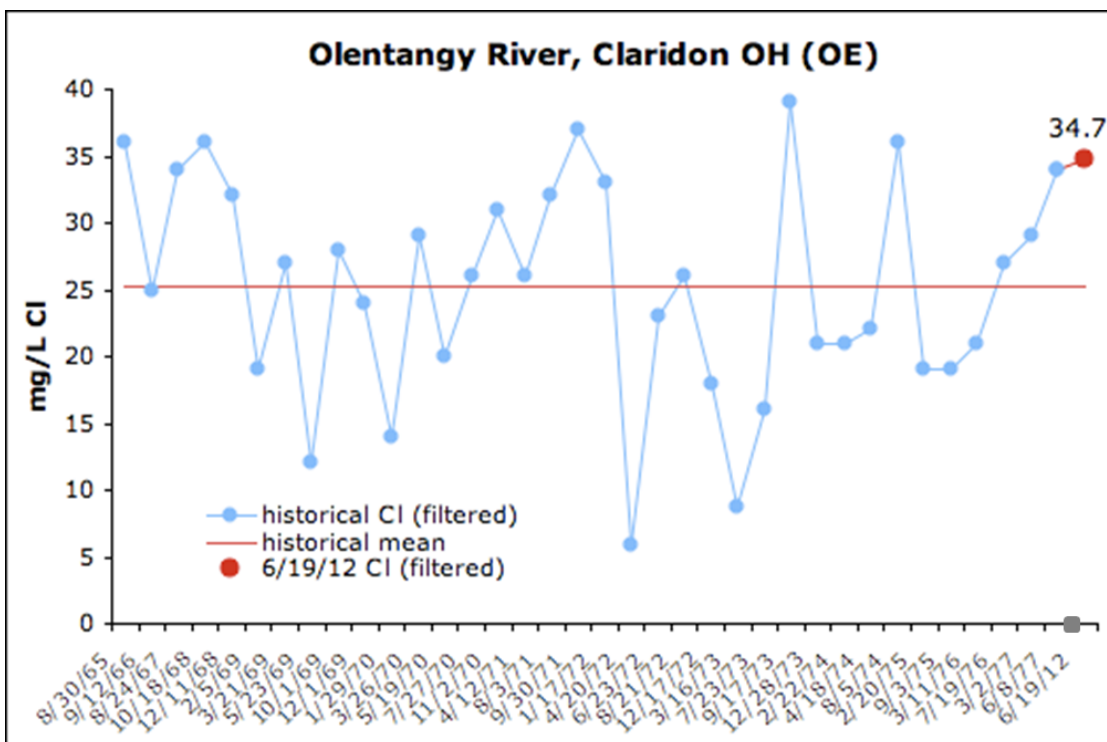


Figure 3b. Time series of chloride concentration at Olentangy River, Drake Union & Worthington OH. Historical Data from USGS NWIS site no. 3226800 and Dr. Berry Lyon's research group.

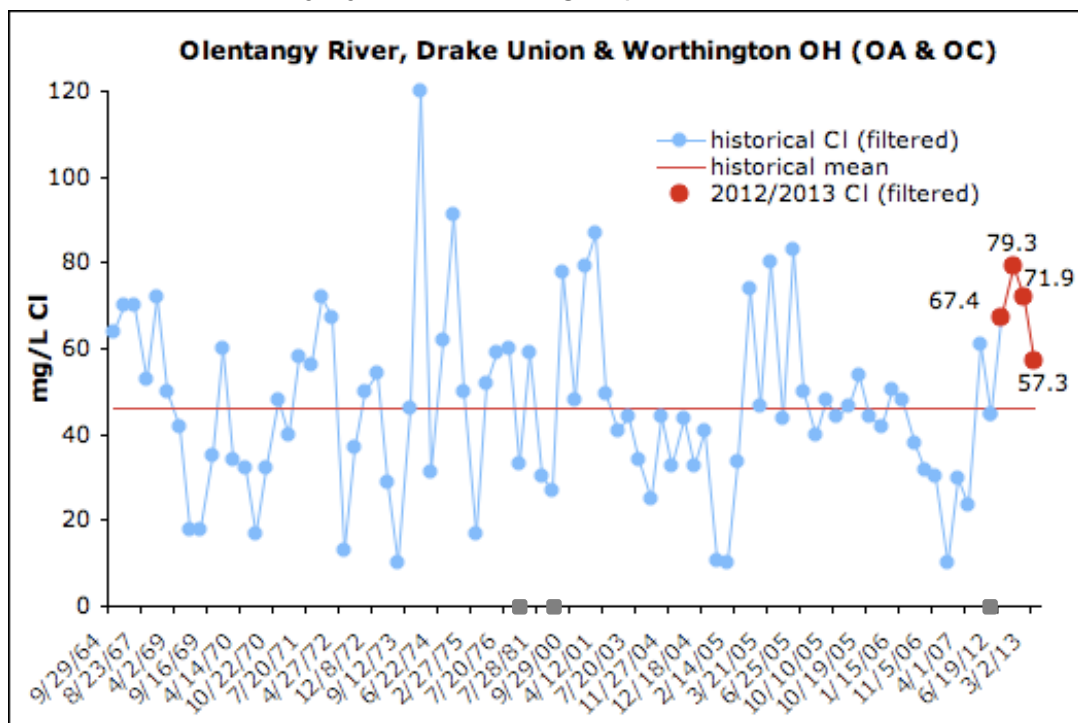


Figure 3c. Time series of nitrate concentration at Olentangy River, Drake Union & Worthington OH. Historical Data from USGS NWIS site no. 3226800 and Dr. Berry Lyon's research group.

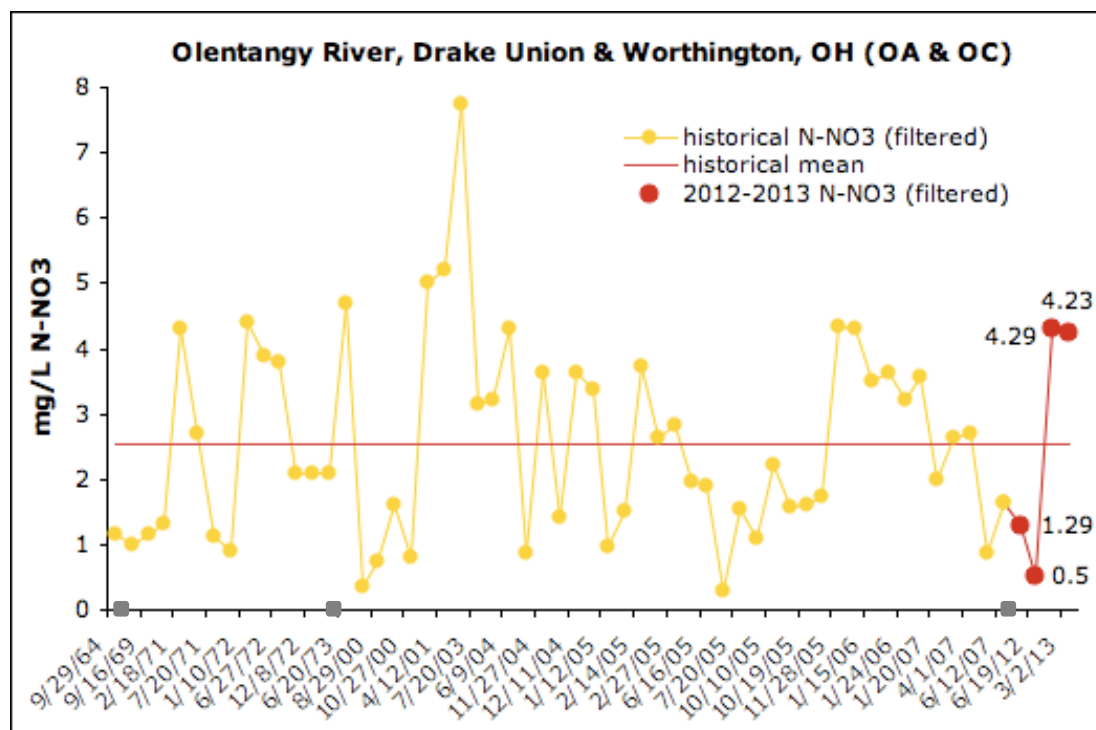


Figure 3d. Time series of sodium concentration at Olentangy River, Worthington OH. Historical Data from USGS NWIS site no. 3226800.

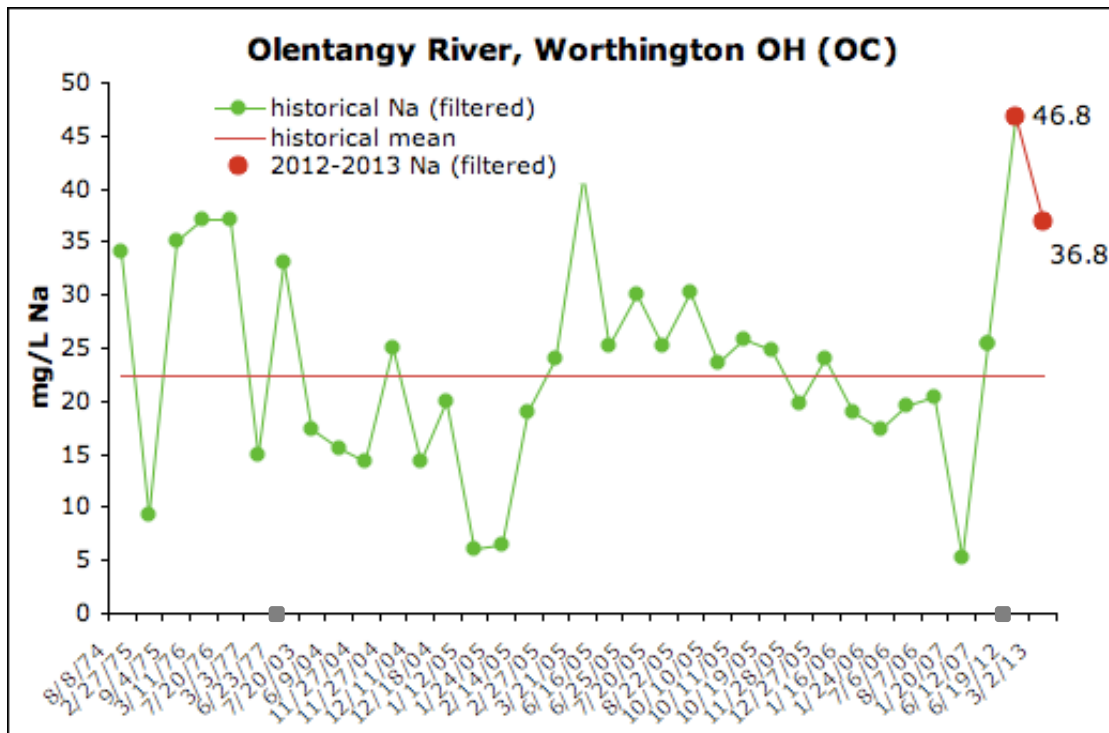


Figure 4a. Time series of chloride concentration at Little Darby Creek, West Jefferson OH. Historical Data from USGS NWIS site no. 3230310 and Dr. Anne Carey's research group.

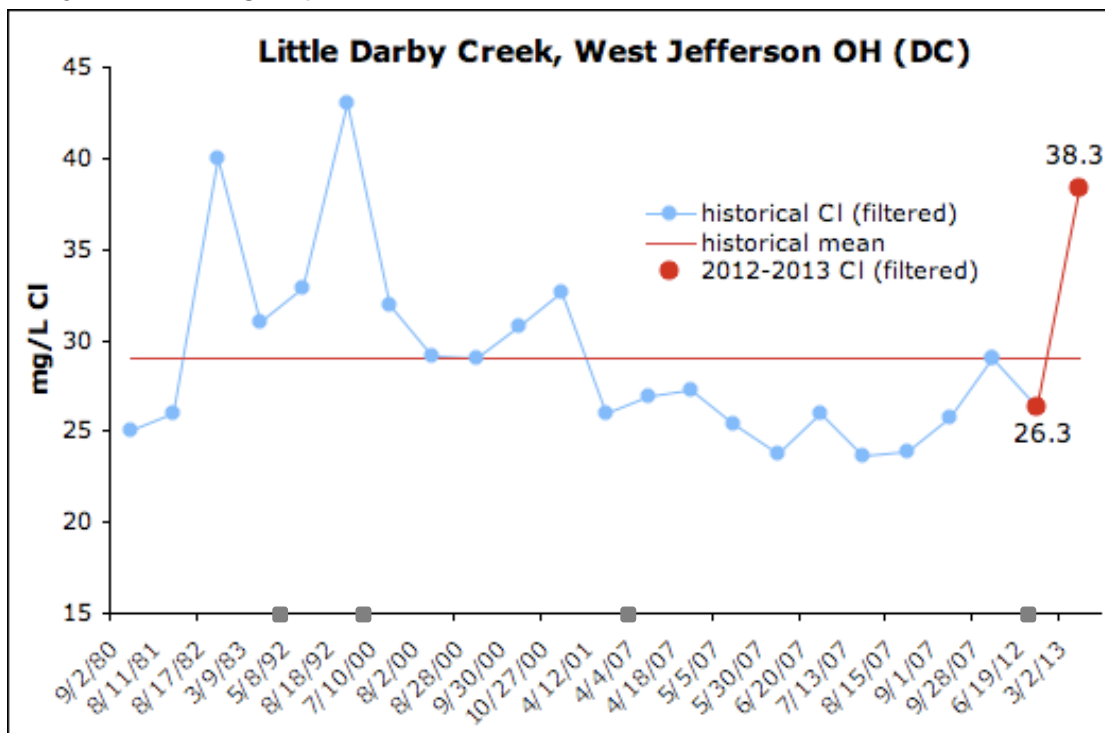


Figure 4b. Time series of nitrate concentration at Little Darby Creek, West Jefferson OH. Historical Data from USGS NWIS site no. 3230310 and Dr. Anne Carey's research group.

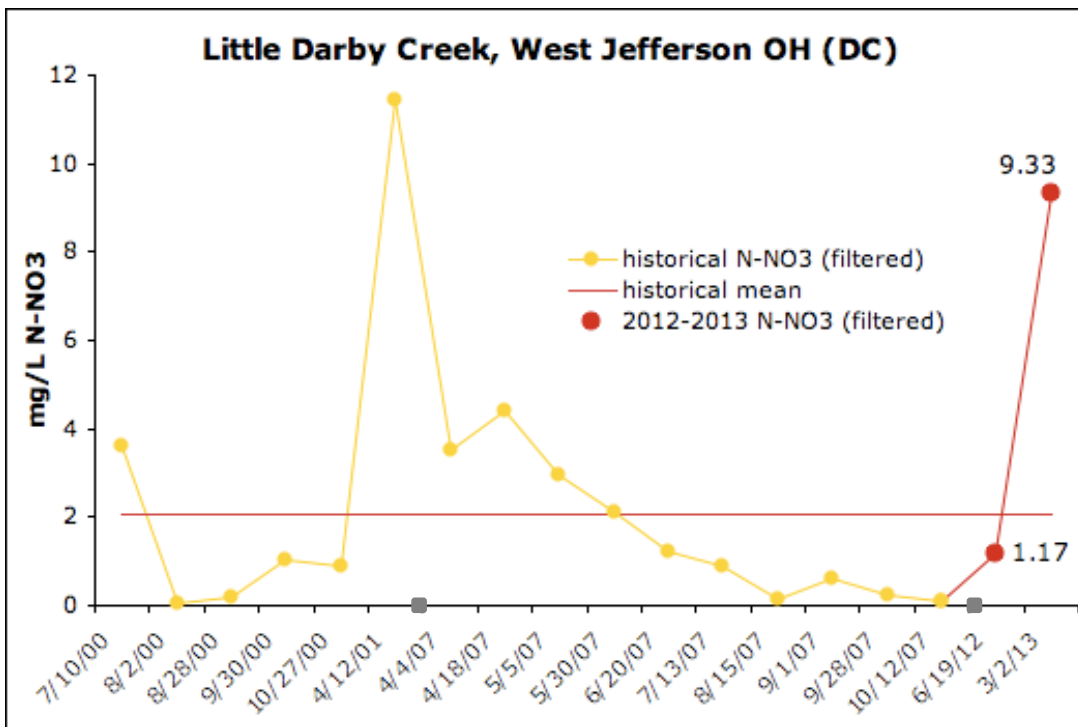


Figure 4c. Time series of chloride concentration at Big Darby Creek, Darbydale OH. Historical Data from USGS NWIS site no. 3230400 and Dr. Anne Carey's research group.

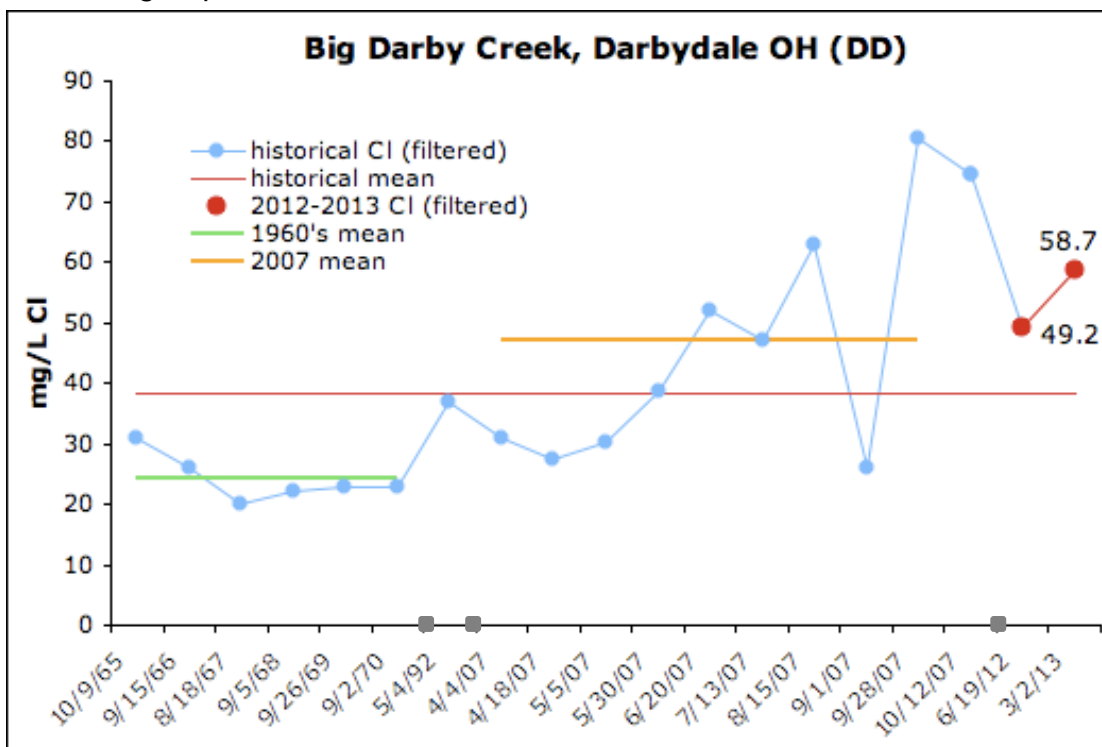


Figure 4d. Time series of nitrate concentration at Big Darby Creek, Darbydale OH. Historical Data from USGS NWIS site no. 3230400 and Dr. Anne Carey's research group.

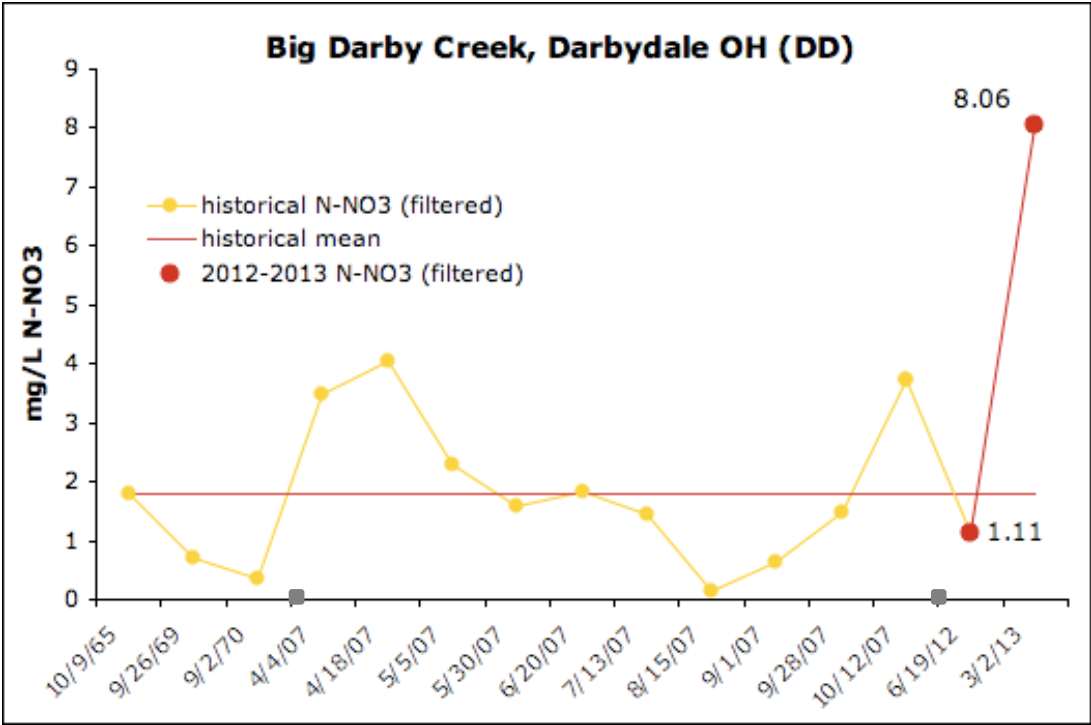


Figure 4e. Time series of chloride concentration at Big Darby Creek, Darbyville OH. Historical Data from USGS NWIS site no. 3230500.

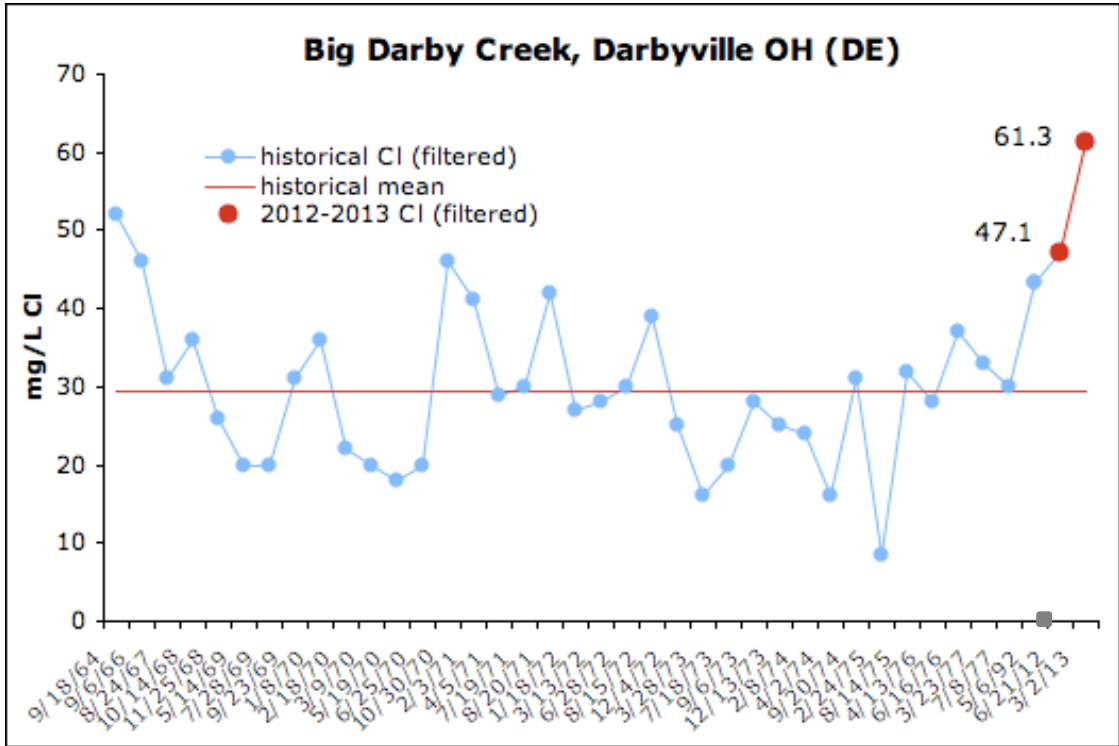


Figure 4f. Time series of nitrate concentration at Big Darby Creek, Darbyville OH. Historical Data from USGS NWIS site no. 3230500.

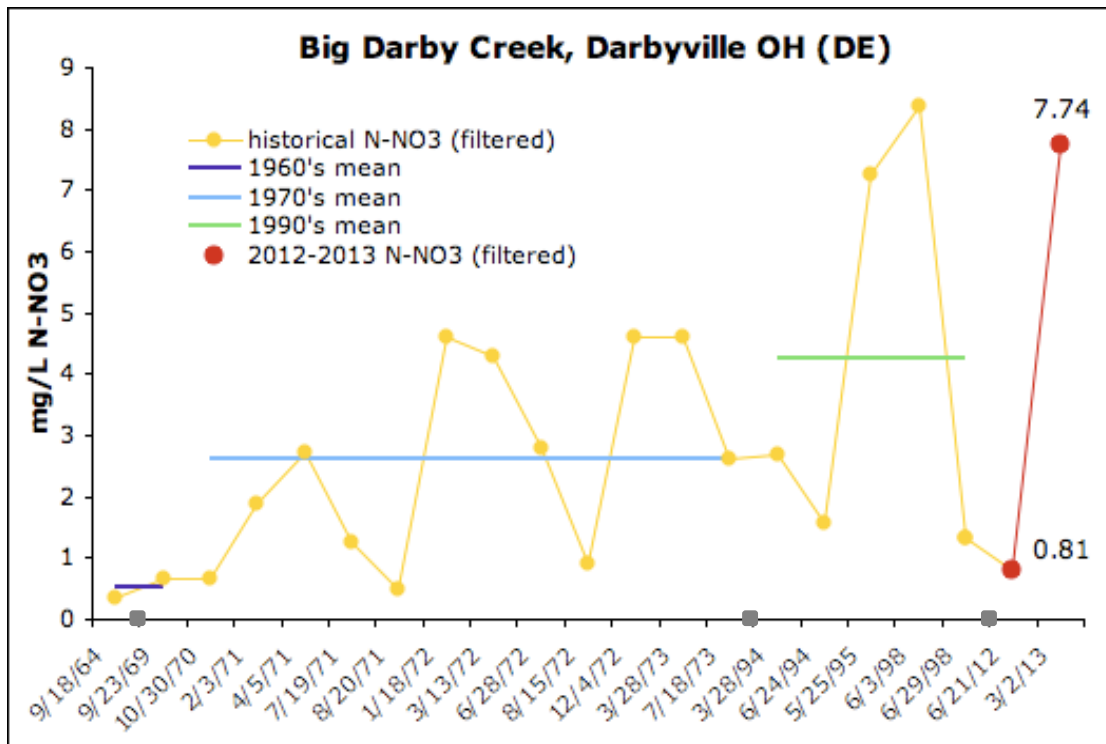


Figure 5a. Time series of chloride concentration at Hocking River, Athens OH. Historical Data from USGS NWIS site no. 3159500.

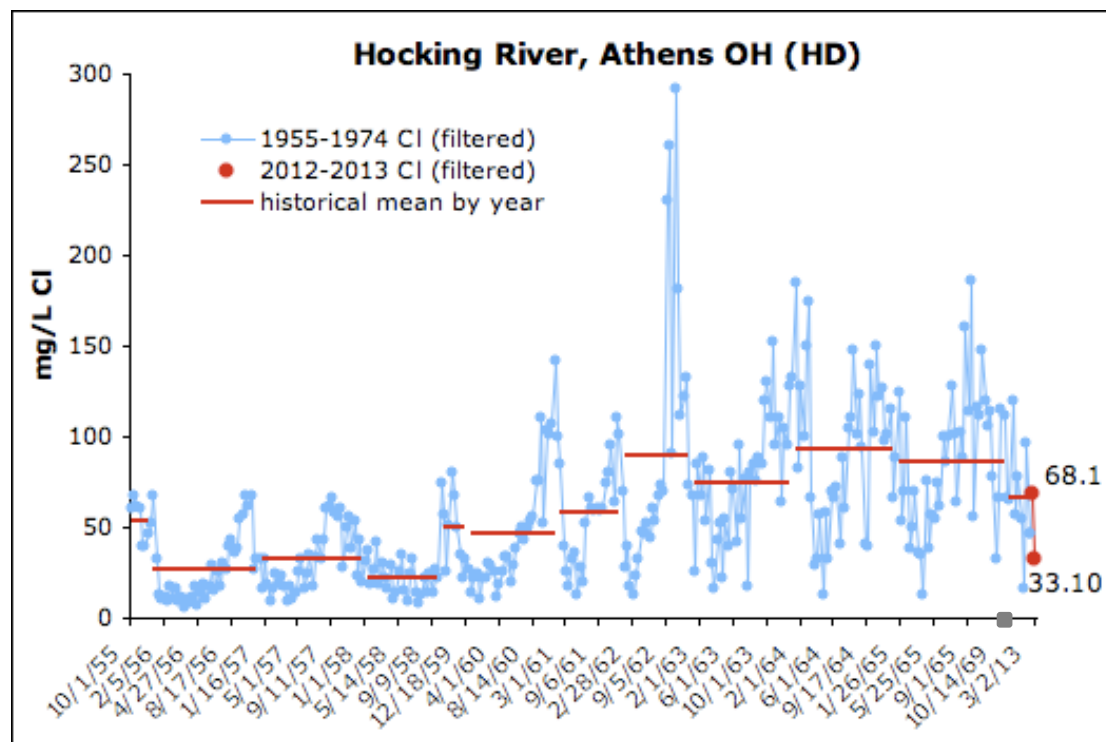


Figure 5b. Time series of sodium concentration at Hocking River, Athens OH. Historical Data from USGS NWIS site no. 3159500.

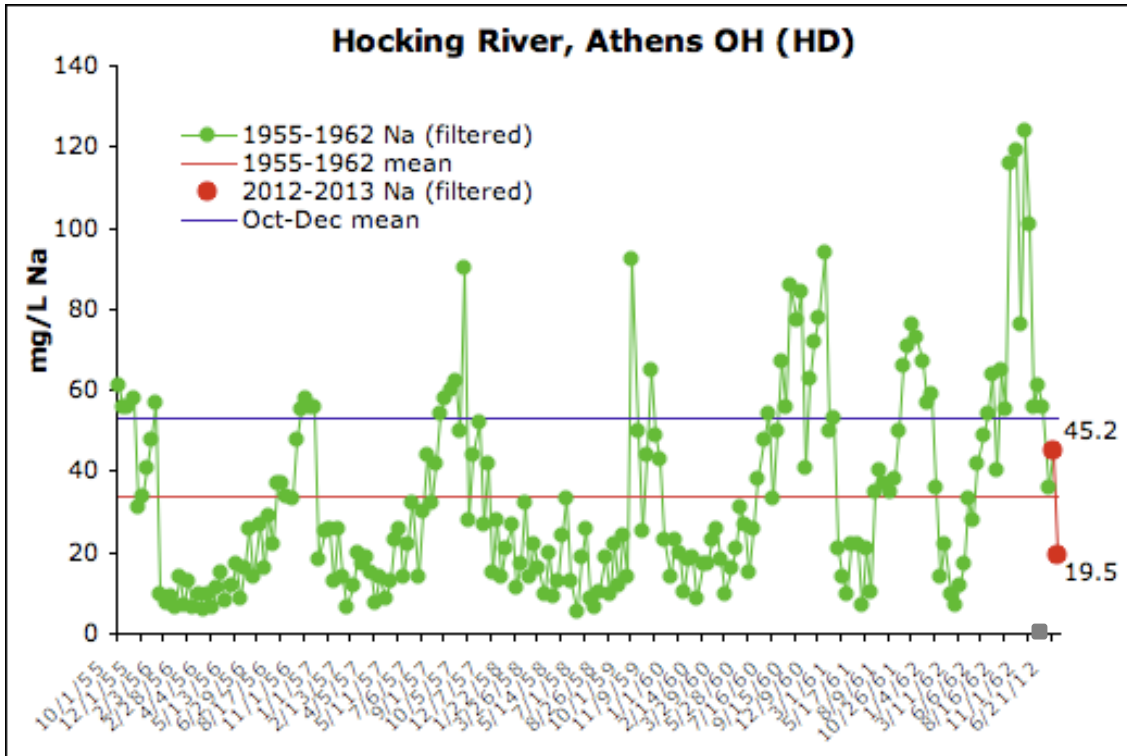


Figure 6a. Time series of nitrate concentration at Little Miami River, Yellow Springs OH. Historical Data from USGS NWIS site no. 3240000.

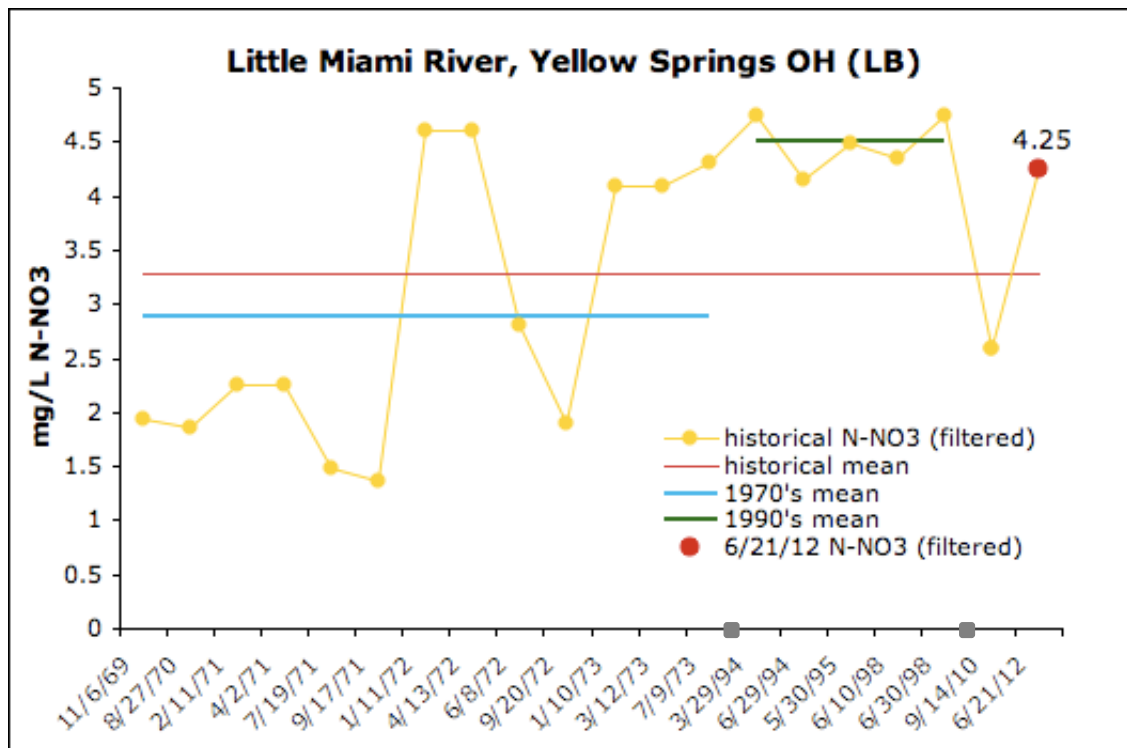


Figure 6b. Time series of chloride concentration at Little Miami River, Milford OH. Historical Data from USGS NWIS site no. 3245500.

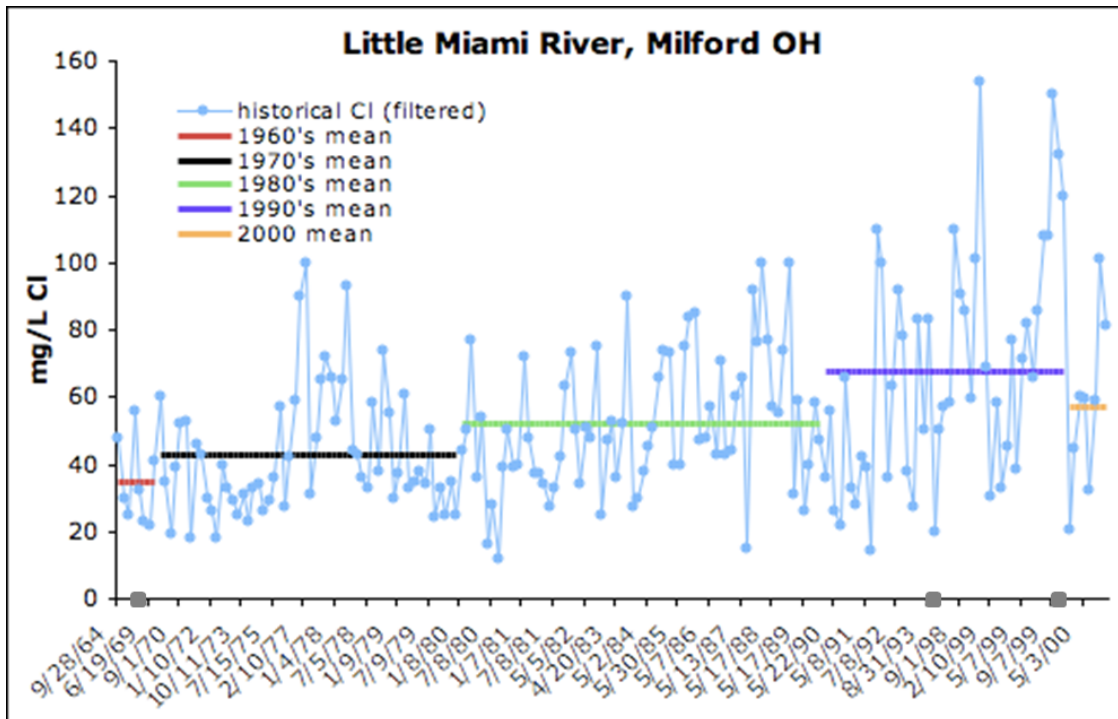
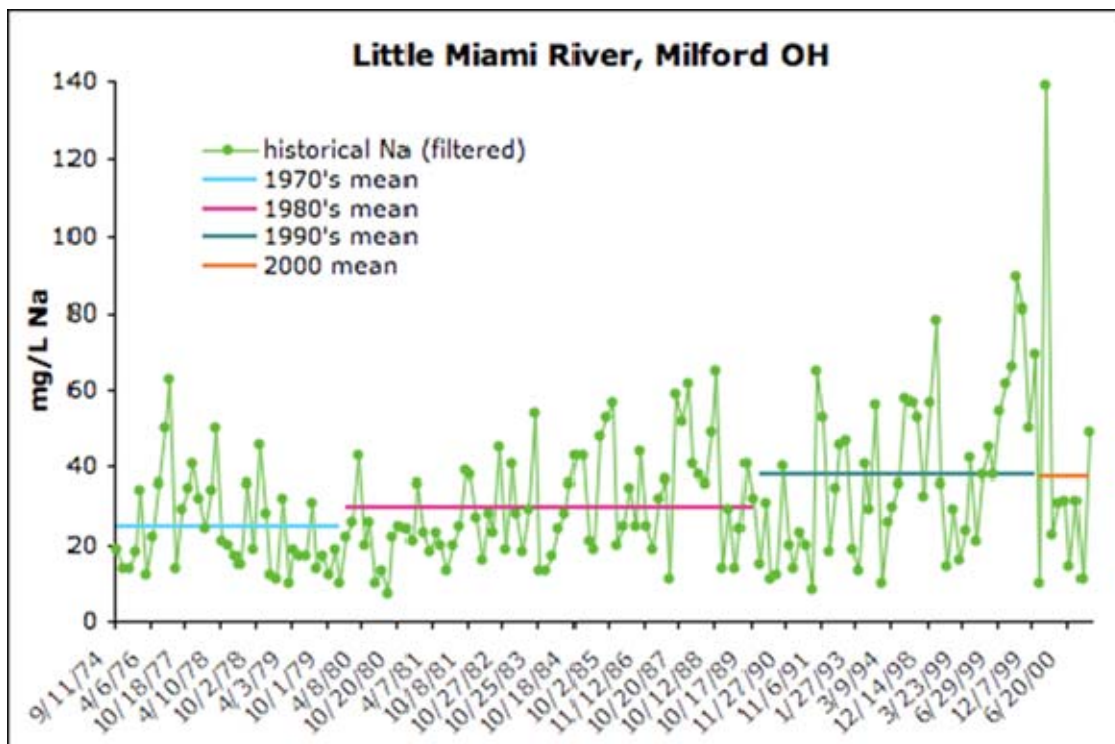


Figure 6c. Time series of sodium concentration at Little Miami River, Milford OH. Historical Data from USGS NWIS site no. 3245500.



Appendix B

Tables

June 2012 Ion Concentrations (mg/L)														Nutrients (ppb)		
Sample ID	Date	Li	Na	K	Mg	Ca	F	Cl	Br	N-NO3	SO4	P-PO4	NH3	SiO2		
OA	6/19/12	0.007	36.9	4.9	17.8	60.9	0.31	67.4	0.037	0.50	79.2	25.6	39.9	3617		
OC	6/19/12	0.012	46.8	7.4	24.9	74.1	0.39	79.3	0.049	1.29	132.9	182.3	55.5	2183		
OD	6/19/12	0.003	12.2	4.6	16.4	55.7	0.22	27.0	0.014	2.51	36.4	16.4	807.9	3587		
OE	6/19/12	0.010	20.8	3.5	25.8	84.3	0.32	34.7	0.030	1.03	72.2	51.1	129.7	7595		
AE	6/19/12	0.010	25.1	5.4	23.0	65.9	0.25	46.0	0.052	7.90	79.0	36.7	57.0	7286		
LB	6/21/12	0.002	8.0	2.6	29.5	78.8	0.25	18.7	0.006	4.25	32.3	54.1	23.7	10907		
DC	6/19/12	0.005	13.0	1.8	34.3	79.3	0.47	26.3	0.008	1.17	45.4	44.6	45.7	10791		
DD	6/19/12	0.005	28.1	2.4	34.3	76.3	0.50	49.2	0.013	1.11	62.1	116.1	62.2	8995		
DE	6/21/12	0.005	27.1	2.5	32.9	75.7	0.48	47.1	0.012	0.81	57.6	102.0	5.4	9468		
DF	6/19/12	0.005	19.0	2.1	33.1	68.4	0.47	33.9	0.006	0.53	56.8	54.1	84.4	9266		
HB	6/21/12	0.007	43.6	3.2	24.3	78.8	0.18	55.0	0.015	0.67	49.5	229.4	63.1	8111		
HC	6/21/12	0.009	29.7	3.3	23.3	73.9	0.18	53.1	0.054	1.56	69.4	34.1	64.5	8352		
HD	6/21/12	0.015	45.2	3.7	24.7	80.2	0.18	68.1	0.113	0.50	151.4	0.9	33.6	7391		

March 2013 Ion Concentrations (mg/L)													
Sample ID	Date	Li	Na	K	Mg	Ca	F	Cl	Br	N-NO3	SO4		
OA	3/2/13	0.002	29.1	3.5	14.7	52.9	0.22	57.3	0.013	4.23	42.0		
OC	3/2/13	0.002	36.8	3.5	14.7	51.4	0.21	71.9	0.014	4.29	41.4		
DC	3/2/13	0.002	15.6	1.6	32.3	76.6	0.38	38.3	0.005	9.33	45.9		
DD	3/2/13	0.002	28.8	2.4	28.1	68.9	0.35	58.7	0.007	8.06	41.2		
DE	3/2/13	0.002	30.1	2.5	26.7	64.7	0.31	61.3	0.006	7.74	39.5		
HA	3/2/13	0.003	20.6	2.2	14.7	43.6	0.13	40.7	0.034	2.73	48.6		
HB	3/2/13	0.002	39.0	2.3	23.8	73.6	0.17	71.1	0.014	4.05	57.1		
HD	3/2/13	0.004	19.5	2.0	12.7	37.9	0.13	33.1	0.040	1.68	64.2		

Table 3													
June 2012													
Sample ID	Li mg/L	Na mg/L	K mg/L	Mg mg/L	Ca mg/L	Sample ID	F mg/L	Cl mg/L	Br mg/L	N-NO3 mg/L	SO4 mg/L		
AE	0.01	25.1	5.39	23.1	66.0	AE	0.23	46.1	0.05	7.86	78.7		
AE duplicate	0.01	25.1	5.40	23.0	65.8	AE duplicate	0.26	45.8	0.05	7.94	79.4		
% difference	0.08	0.20	0.17	0.44	0.26	% difference	14.1	0.69	1.25	0.95	0.96		
Sample ID	Li mg/L	Na mg/L	K mg/L	Mg mg/L	Ca mg/L	Sample ID	F mg/L	Cl mg/L	Br mg/L	N-NO3 mg/L	SO4 mg/L		
DF	0.01	19.0	2.08	33.1	68.3	DF	0.51	33.9	0.01	0.54	57.0		
DF duplicate	0.01	19.0	2.09	33.1	68.6	DF duplicate	0.44	34.0	0.01	0.51	56.5		
% difference	9.13	0.03	0.43	0.04	0.37	% difference	12.9	0.24	22.1	5.39	0.94		

March 2013													
Sample ID	Li mg/L	Na mg/L	K mg/L	Mg mg/L	Ca mg/L	Sample ID	F mg/L	Cl mg/L	Br mg/L	N-NO3 mg/L	SO4 mg/L		
DD	0.002	28.8	2.43	28.0	68.7	DC	0.40	38.3	0.006	9.33	45.8		
DD duplicate	0.002	28.8	2.41	28.2	69.0	DC duplicate	0.37	38.2	0.005	9.33	46.0		
% difference	0.02	0.10	1.11	0.83	0.33	% difference	6.81	0.28	25.2	0.00	0.47		
Sample ID	Li mg/L	Na mg/L	K mg/L	Mg mg/L	Ca mg/L	Sample ID	F mg/L	Cl mg/L	Br mg/L	N-NO3 mg/L	SO4 mg/L		
HD	0.004	20.1	2.03	12.9	38.7	HB	0.17	71.1	0.01	4.06	57.2		
HD duplicate	0.004	19.0	1.89	12.4	37.1	HB duplicate	0.17	71.1	0.01	4.04	56.9		
% difference	10.7	5.27	6.62	4.25	4.16	% difference	3.79	0.01	9.94	0.44	0.54		

